Ultrafast Bimolecular Reaction Kinetics between S$_1$ *trans*-Stilbene and Carbon Tetrachloride Studied by Sub-Picosecond Time-Resolved Visible Absorption Spectroscopy

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Ultrafast bimolecular reaction kinetics between S$_1$ *trans*-stilbene and carbon tetrachloride is monitored by sub-picosecond time-resolved visible absorption spectroscopy. The observed kinetics is well explained either by Smoluchowski's theory or by Collins-Kimball's theory of diffusion-controlled reactions. These results suggest that the molecular motion in solution for a few picosecond time period is well described by diffusion.

When *trans*-stilbene is photoexcited to the first excited singlet (S$_1$) state in a carbon tetrachloride solution, it reacts with the solvent in a few picoseconds.[1] From various spectroscopic observations including the detection of the trichloromethyl radical by time-resolve infrared spectroscopy, we concluded that a Cl atom is transferred from carbon tetrachloride to *trans*-stilbene on the photoexcitation. There have been no experimental results obtained which indicate the complex formation between *trans*-stilbene and carbon tetrachloride, either in the S$_1$ state or in the ground state.[1] From the fluorescence quenching measurements and their temperature dependence, we found that the reaction kinetics was well explained by Smoluchowski's theory of diffusion-controlled reactions, even if this reaction was completed in a few picoseconds.[2] At this time, however, the width of the instrumental response function was about 8 ps. It was not possible to directly fit the observed kinetics with a function derived from the model. In this study, we measure the bimolecular reaction kinetics with a better time resolution of 200 fs by using femtosecond time-resolved visible absorption spectroscopy. This enables us to compare the observed reaction kinetics with the model function in a direct way.

Time dependence of the S$_n$-S$_1$ absorption intensity of *trans*-stilbene in carbon tetrachloride was measured with a femtosecond time-resolved visible absorption spectrometer. The details of the spectrometer were reported elsewhere.[3] White light continuum generated by amplified output of a home-made self-mode-locked Ti:sapphire laser was used as a probe pulse while the third harmonic of the amplified output (270 nm) was used as a pump pulse. The S$_n$-S$_1$ absorption of *trans*-stilbene was monitored at 590 nm. The angle between the pump polarization and the probe polarization was set to be 55 degrees. Three different sample concentrations were tried between 2.8 x 10^{-3} and 5.6 x 10^{-3} mol dm^{-3}. There was no difference observed, beyond the experimental uncertainties, among these three samples.

The kinetics of diffusion-controlled reactions have been studied by various groups theoretically[4-8] and experimentally.[9,10] When the S$_1$ state of *trans*-stilbene is quenched by the reaction with carbon tetrachloride, concentration of the S$_1$ state at time *t*, *N(t)*, is described in general as,

$$N(t) = N(0)\exp\left(-\int k(t)[CCl_4]\,dt\right) \qquad (1)$$

where *k(t)* is a time-dependent second-order rate constant and $N(0)$ is the concentration at the photoexcitation (t=0). Smoluchowski's theory of diffusion-controlled reactions[4] gives a simple and basic form for the rate constant *k(t)*,

$$k(t) = 4\pi R N_A D\left(1 + \frac{R}{\sqrt{\pi D t}}\right) \qquad (2)$$

where *D* is the relative diffusion coefficient, N_A is the Avogadro number, and *R* is a distance between the center of the solute and the boundary where the reaction occurs. If a reactant molecule reaches the distance *R* from the other reactant, the two molecules react with a unit probability.

We fitted the observed population decay of S$_1$ *trans*-stilbene with the model function (Eqs 1 and 2). The fitting parameter was the distance *R*. Molar concentration of pure carbon tetrachloride (10.36 mol dm^{-3}) was used for [CCl$_4$]. Relative diffusion coefficient *D* was estimated to be 2.3 x 10^{-9} m^{2}s^{-1} from the reported diffusion coefficient of carbon tetrachloride[11] and the ratio of the molecualr volumes of carbon tetrachloride and *trans*-stilbene.[2] The results are shown in Figure 1. The agreement between the observation and the fitted function is satisfactory. The best fit was obtained when *R* was 0.42 nm.
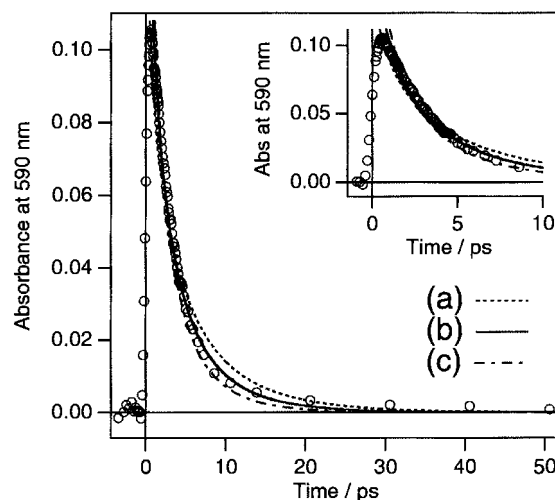

Figure 1. Observed quenching kinetics of S$_1$ *trans*-stilbene in carbon tetrachloride (open circles). Quenching kinetics simulated by Smoluchowski's theory are also shown for *R*=0.37 nm (a), *R*=0.42 nm (b, best fit), and *R*=0.47 nm (c). Relative diffusion coefficient *D* (=2.28 x 10^{-9} m^{2}s^{-1}), estimated from the literature value, was used throughout the fitting procedure. Early time kinetics are shown with an expanded horizontal scale at the upper right corner.

The molecular volume of *trans*-stilbene calculated from its density is 0.309 nm³. This volume corresponds to a sphere with the radius of 0.42 nm. If we assume a facial or hexagonal closest packing, the filling factor should be 0.740. In this case, the radius is estimated to be 0.38 nm. The agreement of the radius evaluated from the molecular volume is close to the fitted R value.

For modifying Smoluchowski's theory, Collins and Kimball introduced a variable bimolecular reaction probability when the distance of the reactants reaches R.[5] In this approach, apparent bimolecular rate constant is[12],

$$k(t) = \frac{4\pi R N_A D k_{act}}{4\pi R N_A D + k_{act}} \left[1 + \frac{k_{act}}{4\pi R N_A D} \exp\left[\frac{Dt}{R^2}\left(1 + \frac{k_{act}}{4\pi R N_A D}\right)^2 \right] \right]$$

$$\times erfc\left[\frac{\sqrt{Dt}}{R}\left(1 + \frac{k_{act}}{4\pi R N_A D}\right) \right] \qquad (3)$$

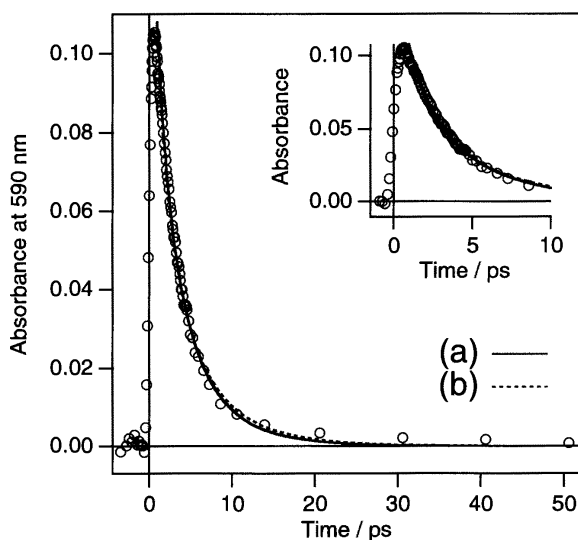where k_{act} is the rate constant when the two reactants reach the distance R.

Figure 2. Observed quenching kinetics of S_1 *trans*-stilbene in carbon tetrachloride (open circles) and simulated kinetics by Collins and Kimball's theory (a). Simulated curve by Smoluchowski's theory (R=0.42 nm) is also shown for reference in (b). Early time kinetics are shown with an expanded horizontal scale at the upper right corner.

The observed decay kinetics is explained by using the rate constant in Eq. 3 as well. The results are shown in Figure 2. In the figure, the best fit with the second model function (Eqs 1 and 3) is shown with the solid curve. The agreement between the model function and the observed curve is again satisfactory. The best fit was obtained when R is 0.50 nm and k_{act} is 7×10^{10} mol⁻¹ dm³ s⁻¹. The new R value is also realistic. The obtained k_{act} value is quite large for a bimolecular rate constant and usually it is difficult to measure such a large rate constant in solution because the slower diffusion process reduces the apparent reaction rate.

In conclusion, the observed fast bimolecular reaction rate between the S_1 state of *trans*-stilbene and carbon tetrachloride is well explained by diffusion-controlled reaction models. This suggests that the molecular motion in solution is successfully described as diffusion even in the short time period of a few picoseconds.

References and Notes
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